Towards a Unified Formulation of Microrheological models

BY

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1. Introduction

In the theories about the rheological behaviour of materials their actual state is to represented by a model. Such a model may be considered an image of the system, simplified in such a way that it is tractable for mathematical analysis and still representing the features of the system that are expected to be important for its rheological behaviour. The development of models may be viewed as a process in which some kind of balance between physical reality, mathematical simplicity and usefulness is optimized.

In the present paper a thermodynamic approach is given which may be applied to many type of models in a unified and systematic way. Our results are similar to the ones obtained earlier by Lhuillier [1] and Maugin and Drout [2], but derived in a slightly different manner and generalized to a broader class of systems. There is also a close connection with the more general abstract formulation of Grmela [3] based upon a bracket formulation of diffusion and convection equations. In the work of Grmela however the general matrix representation (see eq. (2.7) below) which plays a central role in our formulation was not obtained. An important notion in our approach is the explicit distinguishment of different levels of description. This means that the representation of system by a model may be a more or less detailed description of the real microstructure. The following levels of description may be considered:

level 1: molecular dynamics

A molecular model representation very similar to the real microstucture and governed by classical mechanics. This level is used in computer simulations.

level 2: phase space
Representation of the structure like level 1, but specification of the state by a distribution function in phase space.

level 3: configuration space
Representation of the structure like level 2 but preaveraged with respect to velocities. The state is specified by a configurational distribution function.

level 4: structural variables
The structure is represented by a (set of) scalar and/or tensorial variables.

level 5: continuum
The system is represented by a continuum, specified by (a) constitutive equation(s).

In the present paper we will consider only the levels 3, 4 and 5. Nevertheless there will be still many possible descriptions for each system. The reason for this is that, as we shall see in the next section, the model is based upon a division of the system in a subsystem and its environment, both of which may be described at different levels of description.

In section 2 the general theory -which, for reasons to be given in section 3.1, will be called "the triangle model" -will be presented and in section 3 the application to a number of rheological models will be discussed. These applications are merely to illustrate the method. No attempt has been made to be complete in some sense or to obtain new results. In section 4 we discuss some features of the present approach and some prospects for future investigations.

2. Theory

In any microrheological model it is possible to define a subsystem and a set of external stresses and forces are acting on it. This set will be denoted here by Σ, and the associated set of external flows and velocities by $\dot{\Gamma}$. The power supply to the subsystem then becomes

$$W = \Sigma \cdot \dot{\Gamma} \qquad (2.1)$$

Here, the dot denotes an inner product in the linear space to which Σ and $\dot{\Gamma}$ belong. If Σ and $\dot{\Gamma}$ are vectors or tensors the product will be a single or multiple contrac-

tion. Σ and $\dot{\Gamma}$ may however also denote spatial fields or other functions, in that case the inner product in (1) may contain an integration with respect to the space coordinates or other variables.

Besides the external variables Σ and $\dot{\Gamma}$ we introduce a set of state variables Φ, such that, at constant temperature, the free energy A of the system may be expressed as a function, or a functional of Φ:

$$A = A\ (\Phi) \tag{2.2}$$

The derivative of A with respect to Φ has the significance of a (set of) thermodynamic force(s):

$$\Pi = \frac{\delta A}{\delta \Phi} = \Pi\ (\Phi) \tag{2.3}$$

Here, and elsewhere in this paper, the kind of derivative is not explicitly specified, it depends upon the nature of the quantity Φ: if Φ is a set of scalar or tensorial variables (3) consists of a set of partial derivatives and in the case that Φ is a function, an apropriate functional derivative. The latter situation occurs, for instance in configurational-space molecular models, if the distribution function ψ is used as the state variable Φ.

We now consider the rate of dissipation Δ. Bij definition, this is the power supply (1) minus the rate of reversible storage of energy. In the isothermal case, the latter part equals the rate of change of the free energy $\dot{A} = \Pi * \dot{\Phi}$ (the * denotes an inner product in the space to which Π and Φ belong) so we have

$$\Delta = \Sigma \cdot \dot{\Gamma} - \Pi * \dot{\Phi} \tag{2.4}$$

We assume that the set of variables, introduced so far, is complete in the sense that all quantities in (4) may be considered as functions (or functionals) of $\dot{\Gamma}$ and Π:

$$\Sigma = \Sigma\ (\dot{\Gamma}, \Pi) \quad , \quad \dot{\Phi} = \dot{\Phi}\ (\dot{\Gamma}, \Pi) \tag{2.5}$$

If from the three equations (4) and (5) the internal variables Π and Φ (including $\dot{\Phi}$) are eliminated a relation between Σ and $\dot{\Gamma}$ results. This is the microscopic constitutive equation of the model.

We will now impose some general restrictions upon the functionals (5). To that end we introduce the concept of a "macroscopic time reversal". With this we mean a reversal of the external flows and velocities. The term "macroscopic" is used, in order to distinguish this kind of time reversal from a real time reversal in which also on a

microscopic scale all velocities and rates of change of state variables are reversed A microscopic time reversal implies a macroscopic one but the opposite statement is not necessarily true. In the present formalism a macroscopic time reversal is a change of sign of the variable $\dot{\Gamma}$. Under such a transformation the variables Δ, Σ, π and $\dot{\Phi}$ will also change but some restrictions upon these changes are imposed by the laws of thermodynamics. In order to analyse this, we define for any functional $f(\dot{\Gamma})$ an even and an odd part with respect to macroscopic time reversal as

$$f^{+}(\dot{\Gamma}) + \frac{1}{2}(f(\dot{\Gamma}) + f(-\dot{\Gamma})) \quad \text{and} \quad f^{-}(\dot{\Gamma}) = \frac{1}{2}(f(\dot{\Gamma}) - f(-\dot{\Gamma}))$$

For the variables in (4) we then have: $\Delta = \Delta^{+}$, since the dissipation Δ has to be positive, by the second law of thermodynamics; $\dot{\Gamma} = \dot{\Gamma}^{-}$, by definition; and $\Pi = \Pi^{+}$, since according to (3) Π is a variable of state and not directly dependent upon $\dot{\Gamma}$. The quantities Σ and $\dot{\Phi}$ have no definite parity, so, in general: $\Sigma = \Sigma^{+} + \Sigma^{-}$ and $\dot{\Phi} = \dot{\Phi}^{-} + \dot{\Phi}^{+}$.

We now consider the even part of (4):

$$\Delta = \Sigma^{-} \cdot \dot{\Gamma} \qquad - \Pi * \dot{\Phi}^{+} \tag{2.6}$$

and the odd part:

$$0 = \Sigma^{+} \cdot \dot{\Gamma} - \Pi * \dot{\Phi}^{-} \tag{2.7}$$

From (6) we see that only the odd part of Σ and the even part of $\dot{\Phi}$ contribute to the dissipation Δ. Therefore we define the dissipative stress Σ^{D} as

$$\Sigma^{D} = \Sigma^{-} \tag{2.8}$$

The even part of Σ will considered as a reversible stress:

$$\Sigma^{R} = \Sigma^{+} \tag{2.9}$$

Similarly we define $\Phi = \dot{\Phi}^{D} + \dot{\Phi}^{R}$

with

$$\dot{\Phi}^{D} = \dot{\Phi}^{+} \tag{2.10}$$

and

$$\dot{\Phi}^{R} = \dot{\Phi}^{-} \tag{2.11}$$

We now will derive some more explicit results about the dependence of Σ and $\dot{\Phi}$ on $\dot{\Gamma}$ and Π. From the parity of $\dot{\Gamma}$, Π, Σ^{D} and $\dot{\Phi}^{D}$, as defined in (8) - (11) it can be seen that we may write:

$$\Sigma^{D} = \eta(\dot{\Gamma}, \Pi) \cdot \dot{\Gamma} \tag{2.12}$$

and

$$\dot{\Phi}^{D} = -\beta(\dot{\Gamma}, \Pi) * \Pi \tag{2.13}$$

in which the quantities η and β are even with respect to $\dot{\Gamma}$. The minus sign in (13) will be explained after eq. (17), below. For the reversible part of $\dot{\Phi}$ we may write

$$\dot{\Phi}^R = \Lambda\ (\dot{\Gamma},\ \Pi) \cdot \dot{\Gamma} \tag{2.14}$$

in which Λ is even with respect to $\dot{\Gamma}$ and Π. If (14) is substituted in (7), on using (9) and (11) we see that

$$\Sigma^R \cdot \dot{\Gamma} = \Pi * \Lambda\ (\dot{\Gamma},\ \Pi) \cdot \dot{\Gamma} \tag{2.15}$$

so

$$\Sigma^R = \Lambda^T\ (\dot{\Gamma},\ \Pi) * \Pi \tag{2.16}$$

The quantity Λ^T in this expression is the adjoint of the operator Λ, in the sense that $\Pi * \Lambda \cdot \dot{\Gamma} = \dot{\Gamma} \cdot \Lambda^T * \Pi$ for arbirary Π and $\dot{\Gamma}$. (In the case that Λ is a tensor, Λ^T denotes the transposed of Λ). The transposed of higher order tensors, defined in this way depends upon the number of contractions corresponding to the products "*" and "·". If, for instance $\underline{\lambda}$ is a third order tensor $\underline{a} \cdot \underline{\lambda} : \underline{B} = \underline{B} : \underline{\lambda}^T \cdot \underline{a}$ implies that $\lambda_{ijk} = \lambda^T{}_{jki}$ whereas $\underline{A} : \underline{\lambda} \cdot \underline{b} = \underline{b} \cdot \underline{\lambda}^T : \underline{A}$ would imply $\lambda_{ijk} = \lambda^T{}_{kij}$. We will make no distinction in the notation of these type of transpositions since in our case their meaning can always be deduced easily from the expressions in which they are used.

We see that, as a direct result of eq. (7), which was obtained by considering the parity of the quantities in (4) with respect to macroscopic time reversal, obtain a close relationship between the evalution equation (14) of $\dot{\Phi}^R$ and the expression (16) of Σ^R.

The results (12), (13), (14) and (16) may be collected in a matrix expression, similar to the one obtained in classical treatment of non-equilibrium thermodynamics from the expression of the entropy production, (which, in the isothermal case considered here, is proportional to the dissipation (4)).

This matrix expression becomes:

$$\begin{bmatrix} \Sigma \\ \dot{\Phi} \end{bmatrix} \qquad \begin{bmatrix} \eta \cdot & -\Lambda^T * \\ \Lambda \cdot & \beta\ * \end{bmatrix} \qquad \begin{bmatrix} \dot{\Gamma} \\ -\Pi \end{bmatrix} \tag{2.17}$$

The skew-semmetry of the off diagonal elements is in accordance with the Onsager-Casimir reciprocal relations. The minus sign in (17) was introduced, in order to use the "forces" and "fluxes" of the expression of the dissipation (4), written as $\Delta = \Sigma \cdot \dot{\Gamma} + (-\Pi) * \dot{\Phi}$.

A derivation of a set of rate equations similar to our derivation of (17) by taking into account the time-reversal properties of dissipative effects was first applied to rheological models by Lhuillier [1], (see also the review article by Maugin and Drout [2]).

The main difference to the approach in these papers and the one presented here is that we do not consider the parity of variables with respect to ordinary time reversal but to what was called a macroscopic time reversal. This enabled us to split up the original expression (4) of the dissipation into the two parts (6) and (7). In this way the reversible and dissipative parts of the quantities $\dot{\Phi}$ amd Σ may be defined in an unambigious way. In the method based upon ordinary time reversal-symmetry a dissipation expression similar to (6) and an expression similar to (7) are introduced ad hoc.

It is interesting to note that since Λ is independent of $\dot{\Gamma}$, if follows from (17) $\Lambda = \delta \dot{\Phi}^R / \delta \dot{\Gamma}$ and so we obtain

$$\Sigma^R = \Pi * \frac{\delta \dot{\Phi}^R}{\delta \dot{\Gamma}} \qquad (2.18)$$

This result is in accordance with an expression first derived by Grmela [3] in a general theory based upon a bracket formulation of convection and diffusion equations. In [3] and also in subsequent publications by Grmela et al. [4-6] it was shown that the expression (18) is consistent with the stress-tensor expressions in many rheological models.
In the application to specific rheological models it is possible to make different choices for the variables Σ, $\dot{\Gamma}$, Π and Φ, depending upon the choice of the sub(system) and the level of description. A particular choice will be referred to as the "(Σ, $\dot{\Gamma}$, / Π, $\dot{\Phi}$) - level of description" with the choosen variables substituted for Σ, $\dot{\Gamma}$, Π and $\dot{\Phi}$ In section 3 we will discuss several rheological models at various levels of description.

3. Applications

The theory, described in section 2 will now be applied to a number of special rheological models. In section 3.1 we start with the treatment of spring dashpot models. This results in the construction of a special type of mechanical model, called "the triangle model" which represents the important features of the general theory in a

schematic way. In section 3.2 the elastic dumbbell will be discussed at several levels of description and in section 3.3. the rigid dumbbell model as an example of a model with a constraint.

In section 3.4 it will be shown that it is also possible to describe reptation models in the present formalism and in section 3.5 we discuss the transient-network model as an example of a kinetic model. Finally in section 3.6 some examples of configurational tensor theories will be treated.

3.1 Mechanical models

In the treatment of linear viscoelasticity one often makes use of spring-dashpot models, as a phenomenological, representation of material behaviour. Although the theory presented in section 2 is not restricted to linear viscoelastic behaviour it is still very instructive to apply it to this type of models. The reason for this is that some of the basic elements of the present model: reversible storage of energy, dissipation and conpling of internal parts of the system to the environment are also the basic characteristics of spring-dashpot models.

The external variables Σ and $\dot{\Gamma}$ in (2.17) then become the external stress τ and the external rate of extension $\dot{\gamma}$, so we have:

$$\Sigma = \tau \quad , \quad \dot{\Gamma} = \dot{\gamma} \tag{3.1-1}$$

The mechanical energy, stored in the springs of the model corresponds to the free energy A (Φ) defined in (2.2). We will consider here models with one spring, with spring force σ and an extension ε, so we have:

$$\pi = \sigma \quad , \quad \Phi = \varepsilon \tag{3.1-2}$$

The dissipation expression (2.4) now becomes:

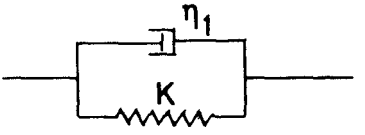
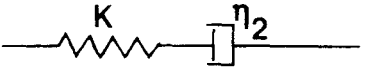
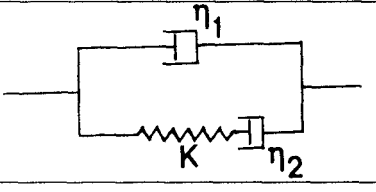
$$\Delta = \tau \dot{\gamma} - \sigma \dot{\varepsilon} \tag{3.1-3}$$

so we, similar to (2.17), we have

$$\begin{bmatrix} \tau \\ \dot{\varepsilon} \end{bmatrix} = \begin{bmatrix} \eta & -\lambda \\ \lambda & \beta \end{bmatrix} \begin{bmatrix} \dot{\gamma} \\ -\sigma \end{bmatrix} \tag{3.1-4}$$

In table 1 the constans η, β and λ are given for a few well known mechanical models. We see that the structure of the matrix in (4) reflects the connection structure of the corresponding network:

Table I
Eq. (3.1-4) applied to some mechanical models

Model	Parameters in ( )		
	η	β	λ
	0	0	1
	η_1	0	1
	0	$1/\eta_2$	1
	η_1	$1/\eta_2$	1

if the internal stress σ is directly coupled to the external stress τ (like in the Maxwell model) the parameter η vanishes. If on the other hand the rate of extension of the spring Σ is directly coupled to the external rate of extension $\dot{\gamma}$ (like in the Voigt-Kelvin model) the parameter β vanishes. the other two possibilities are combinations of these two cases. In all mechanical models discussed so far, we have $\lambda = 1$ The case $\lambda \neq 1$ corresponds to amplification or reduction of stresses and rates of extension in the connection between internal and external variables.
A model in which such is the case is presented in figure 1. This model, which -because of its characteristic shape- will be called "the triangle model", is described by the complete set of equations (4) with $\eta \neq 0$, $\beta \neq 0$ and $\lambda \neq 1$. Since (4)

is similar to the general expression (2.17) the triangle model may be considered also as a symbolic representation of the general theory, described in section 2. For that reason, in the rest of this paper we will also refer to the model described in section 2 as the "triangle theory".

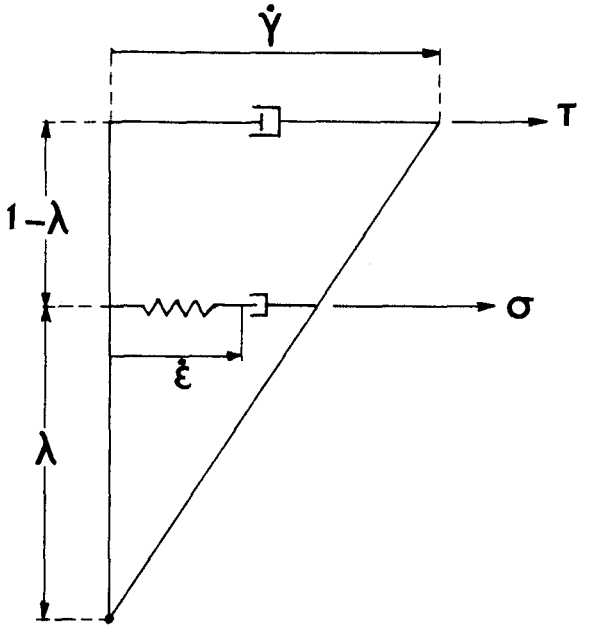


Fig. 1 **The triangle Model**

3.2 The elastic dumbbell model

As a first application of the triangle model to a microscopic model we consider the elastic dumbbell model. This model is used to describe approximately some of the rheological properties of dilute solutions of flexible macromolecules. For an extensive discussion we refer to chapter 13 of ref. [7]. Here we recall that a dumbbell consists of two beads on which hydrodynamic forces are acting, connected by a spring. The spring vector will be denoted by $\underline{q}$ and the configurational distribution function by $\psi(\underline{q}, t)$.

In order to apply the triangle model to the dumbbell model, we first have to define the variables Σ, $\dot{\Gamma}$, Π and Φ. This means that a level of description has to be specified. We start at the ($\underline{T}$, $\underline{L}$/ μ, $\dot{\psi}$)-level, so

$$\Sigma = \underline{T} \quad ; \qquad \dot{\Gamma} = \underline{L}$$
$$\Phi = \psi \quad ; \qquad \Pi = \mu = \frac{\delta A}{\delta \psi} \tag{3.2-1}$$

Here $\underline{T}$ is the macroscopic stress tensor; $\underline{L}$ the velocity gradient tensor and $A = A\{\psi\}$ the free energy, considered as a functional of the distribution function $\psi = \psi\ (\underline{q},t)$. In the present case we have

$$A\{\psi\} = nkT \int \psi \ln \frac{\psi}{\psi_o} \, d^3\zeta \tag{3.2-2}$$

in which n is the number density of dumbbells, k Boltzmanns's constant, T the temperature and ψ_o the equilibrium distribution.
This functional is (within an additative constant) the so called dynamical free energy, introduced by Doi [8]. (see also Sarti and Marrucci [9]).
The associated thermodynamic force, which has the significance of a chemical potential in configuration space becomes

$$\mu = \frac{\delta A}{\delta \psi} = nkT \ (1 + \ln \frac{\psi}{\psi_o}) \tag{3.2-3}$$

The rate of reversible storage of energy due to a change of ψ may now be written as

$$\dot{A} = \frac{\delta A}{\delta \psi} * \frac{\partial \psi}{\partial t} = \int \mu \frac{\partial \psi}{\partial t} \, d^3\underline{q} \tag{3.2-4}$$

On the other hand, the macroscopic power supply is given by the familiar expression $W = \underline{T} : \underline{L}$, so the dissipation becomes:

$$\Delta = \underline{T} : \underline{L} - \mu * \frac{\partial \psi}{\partial t} \tag{3.2-5}$$

For the matrix espression (2.17) we also obtain

$$\begin{bmatrix} \underline{T} \\ \frac{\partial \psi}{\partial t} \end{bmatrix} = \begin{bmatrix} \underline{\eta} : & -\underline{\Lambda}^{T*} \\ \underline{\Lambda} & \beta^* \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\mu \end{bmatrix} \tag{3.2-6}$$

With $\underline{\mu}$ a fourth order tensor, $\underline{\Lambda}$ a second order tensor and β a scalar operator.

In order to determine the explicit forms of these quantities we have to consider the evolution equations and the stress-tensor espressions of the dumbbell model.
First, from the diffusion equation

$$\frac{\partial \psi}{\partial t} = - \frac{\partial}{\partial \underline{q}} \cdot (\psi \, \underline{L} \cdot \underline{q}) + \frac{2}{n\zeta} \frac{\partial}{\partial \underline{q}} \cdot (\psi \frac{\partial}{\partial \underline{q}} \mu) \qquad (3.2\text{-}7)$$

in which ζ is a friction parameter and μ the chemical potential defined by (1), on noting that the first term in the r.h.s of (7) is odd with respect to $\underline{L}$ and the second term is even, we see that the tensor $\underline{\Lambda}$ becomes

$$\underline{\Lambda} = - \frac{\delta}{\delta \underline{q}} (\psi \, \underline{q}) \qquad (3.2\text{-}8)$$

and that the operator β may be represented as

$$\beta = \frac{-2}{n\zeta} \frac{\delta}{\delta \underline{q}} \cdot \psi \frac{\delta}{\delta \underline{q}} \qquad (3.2\text{-}9)$$

It is possible, by using derivatives of the Dirac-delta function to express β in a form such that the last term in (7) becomes of the form $-\beta * \mu$ in which, like in (4) the symbol * denotes an integration in configuration space. We will not use this representation here, and represent β by the differential operator (9). We now consider the stress tensor expression. We first calculate the reversible part from (2) and and (6):

$$\underline{T}^R = \underline{\Lambda}^T * \mu = \mu * \underline{\Lambda} =$$

$$= nkT \int (1 - \ln \frac{\psi}{\psi_o}) (- \frac{\partial}{\partial \underline{q}} \psi \, \underline{q}) \, d^3\underline{q}$$

$$= nkT \int (\frac{\partial}{\partial \underline{q}} \ln \frac{\psi}{\psi_o}) (\psi \, \underline{q}) \, d^3\underline{q}$$

$$= nkT \, \underline{1} + n \langle \underline{f}^I \underline{q} \rangle \qquad (3.2\text{-}10)$$

with $\underline{f}^I = -kT \frac{\partial}{\partial \underline{q}} \ln \psi_o$, the so called connector force. In this way the "Kramers form" of the (reversible part of the) stress tensor is obtained.
The total stress tensor expression for the dumbbell model is given by

$$\underline{T} = 2 \eta \underline{D} - nkT \, \underline{1} + n \langle \underline{f}^I \underline{q} \rangle \qquad (3.2\text{-}11)$$

in which $\underline{D} = \frac{1}{2} (\underline{L} + \underline{L}^T)$. The first term of the r.h.s. is the solvent contribution to the stress tensor. Being odd in $\underline{L}$ this term is the dissipative part $\underline{T}^D$ of $\underline{T}$. So, form (6) and (11) we obtain for the tensor $\underline{\eta}$:

$$\underline{\eta} = 2\eta \, \underline{I} \qquad (3.2\text{-}12)$$

in which $\underline{\underline{I}}$ is a fourth order tensor, defined by

$$I_{ijkm} = \frac{1}{2} (\delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk}) \qquad (3.2\text{-}13)$$

The results (8). (9), (10) and (11) may be collected now in the following matrixs expression:

$$\begin{bmatrix} \underline{\underline{T}} \\ \frac{\partial \psi}{\partial t} \end{bmatrix} = \begin{bmatrix} 2\,\eta \underline{\underline{I}} : & \frac{\partial}{\partial \underline{q}} (\psi\, \underline{q}) * \\ -\frac{\partial}{\partial \underline{q}} (\psi\, \underline{q}): & \frac{-2}{n\zeta} \frac{\partial}{\partial \underline{q}} \cdot \psi \frac{\delta}{\delta \underline{q}} \end{bmatrix} \begin{bmatrix} \underline{\underline{L}} \\ -\mu \end{bmatrix} \qquad (3.2\text{-}14)$$

This result, together with the free energy expression(2) contains all relevant information of the elastic dumbbell model at the present level of description.

We now change to a second level of description. Here we do not take the whole distribution function ψ but the configuration vector $\underline{q}$ as the variable of state. This will be done however in an average sense, namely such that $\dot{\underline{q}}$ is not the actual rapidly fluctuation rate of change of $\underline{q}$ of an individual dumbbell due to the thermal motion, but a flux, proportional to the diffusive flow in configuration space. It is the flux which is also present in the equation of continuity is configuration space:

$$\frac{\partial \psi}{\partial t} = - \frac{\partial}{\partial \underline{q}} \cdot (\psi\, \dot{\underline{q}}) \qquad (3.2\text{-}15)$$

The reversible force, associated with $\underline{q}$ may be obtained by substitution of (15) in (14) and ingretation by parts:

$$\dot{A} = -\int \mu \frac{\partial}{\partial \underline{q}} \cdot (\psi\, \dot{\underline{q}})\, d^3\underline{q} = \int \psi \frac{\partial \mu}{\partial \underline{q}} \cdot \dot{\underline{q}}\, d^3\underline{q} \equiv n < \underline{m} \cdot \dot{\underline{q}} > \qquad (3.2\text{-}16)$$

$$= n < \dot{a} >$$

In this expression $\underline{m}$ is defined as

$$\underline{m} = \frac{1}{n} \frac{\partial \mu}{\partial \underline{q}} = kT \frac{\partial}{\partial \underline{q}} \ln \frac{\psi}{\psi_o}$$

and

$$\dot{a} = \underline{m} \cdot \dot{\underline{q}}$$

The vector $\underline{m}$ is the thermodynamic force associated with the gradient of the chemical potential μ in configuration space. It may also be interpreted as the resultant of minus the Brownian force $\underline{f}^B = -kT \frac{\partial}{\partial \underline{q}} \ln \psi$ and the connector force $\underline{f}^I = - kT \frac{\delta}{\delta \underline{\xi}} \ln \psi_o$.

The quantity $\dot{a}$ in (16) may be considered as a density in configuration space of the

rate of change of the free energy per dumbbell, associated with the flux $\dot{\underline{q}}$ discussed above. This makes it possible to apply the triangle model now to one dumbbell. In that case we have

$$\Pi = \underline{m} \quad , \quad \Phi = \underline{q} \tag{3.2-17}$$

And instead of the total stress tensor $\underline{T}$ we now use the corresponding tensor $\underline{\tau}$, defined by

$$\underline{T} = n \int \psi \, \underline{\tau} \, d^3 = n \langle \underline{\tau} \rangle \tag{3.2-18}$$

The quantity $\underline{\tau}$ will be called a stresslet. The total power supply may be written now as

$$W = \underline{T} : \underline{L} = n \langle \underline{\tau} \rangle : \underline{L} = n \langle w \rangle \tag{3.2-19}$$

with

$$w = \underline{\tau} : \underline{L} \tag{3.2-20}$$

the local density in configuration space, corresponding to the total power W. From (20) we see that in the present description the quantities Σ and $\dot{\Gamma}$ defined in (2.1) become:

$$\Sigma = \underline{\tau} \quad , \quad \dot{\Gamma} = \underline{L} \tag{3.2-21}$$

The matrix representation analogous to (2.17) becomes:

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{q}} \end{bmatrix} = \begin{bmatrix} \underline{\underline{\eta}} : & -\underline{\underline{\Lambda}}^T \cdot \\ \underline{\underline{\Lambda}} : & \underline{\underline{\beta}} \cdot \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m} \end{bmatrix} \tag{3.2-22}$$

In this case $\underline{\eta}$ is a fourth order tensor Λ a third order tensor and $\underline{\beta}$ a second order tensor. The explicit form for these tensors may be obtained from some further properties of the model. First, from the equation of motion

$$\dot{\underline{q}} = \underline{L} \cdot \underline{q} - \frac{2}{\zeta} \underline{m} \tag{3.2-23}$$

in which ζ is a friction coefficient, one obtains

$$\dot{\underline{q}}^R = \underline{L} \cdot \underline{q} = \underline{\underline{\Lambda}} : \underline{L} \tag{3.2-24}$$

so

$$\underline{\underline{\Lambda}} = \underline{\underline{1}} \, \underline{q} \tag{3.2-25}$$

and

$$\dot{\underline{q}}^{D} = -\frac{2}{\zeta}\,\underline{m} = \underline{\beta}\cdot(-\underline{m}) \qquad (3.2\text{-}26)$$

so

$$\underline{\beta} = \frac{2}{\zeta}\,\underline{1} \qquad (3.2\text{-}27)$$

From (22) and (25) we obtain for the reversible part of the stresslet

$$\underline{\tau}^{R} = \underline{\Lambda}^{T}\cdot\underline{m} = \underline{m}\cdot\underline{\Lambda} = \underline{m}\,\underline{q} \qquad (3.2\text{-}28)$$

In accordance with the Kramers form (see form ref. [7])

$$\underline{T}^{R} = n < \underline{m}\underline{q} > = n\,k\,T \int \left(\frac{\partial}{\partial \underline{q}} \ln \frac{\psi}{\psi_{o}}\right) \psi\,\underline{q}\; d^{3}\underline{q} \qquad (3.2\text{-}29)$$

The dissipative part of $\underline{\tau}$ is similar to the first term m (11) given by

$$\underline{\tau}^{D} = \frac{2}{n}\,\eta\,\underline{D} \equiv \underline{\eta} : \underline{L} \qquad (3.2\text{-}30)$$

so

$$\underline{\underline{\eta}} = 2\,\frac{\eta}{n}\,\underline{\underline{I}} \qquad (3.2\text{-}31)$$

with $\underline{\underline{I}}$, given by (13)

The results (25), (26), (28) and (30), collected in matrix form, become:

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{q}} \end{bmatrix} = \begin{bmatrix} \eta\,\underline{\underline{I}} : & -(\underline{1}\underline{q})^{T}\cdot \\ \underline{1}\,\underline{q} : & \frac{2}{\zeta}\,\underline{1}\cdot \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m} \end{bmatrix} \qquad (3.2\text{-}32)$$

Instead of taking $\underline{\tau}$ and $\underline{L}$ as the macroscopic variables in which the external power supply is expressed one also may write

$$W = \underline{f}\cdot\dot{\underline{d}} \qquad (3.2\text{-}33)$$

in which $\underline{f}$ is the hydrodynamic (external) force acting upon a dumbbell and $\dot{\underline{d}} = \underline{L}\cdot\underline{q}$ the relative velocity of the fluid flow at its end points.

The matrix representation (32) then becomes:

$$\begin{bmatrix} \underline{f} \\ \dot{\underline{q}} \end{bmatrix} = \begin{bmatrix} \underline{0} & -\underline{1} \\ \underline{1} & \frac{2}{\zeta}\,\underline{1} \end{bmatrix} \begin{bmatrix} \dot{\underline{d}} \\ -\underline{m} \end{bmatrix} \qquad (3.2\text{-}34)$$

This form expresse the equilibrium of forces : $\underline{f} = \underline{m}$ and the Stokes law $\underline{f} = \frac{\zeta}{2}(\dot{\underline{d}} - \dot{\underline{q}})$. We see that again, the skew symmetry of the off-diagonal elements of the matrix is obeyed. A final description that we will cosider in connection with the elastic dumbbell model is one in terms of the configuration tensor

$$\underline{S} = < \underline{q}\,\underline{q} > \qquad (3.2\text{-}35)$$

as a variable of state. A closed description at that level is possible if the free energy A can be expressed explicitely as a function of $\underline{S}$. In the case of linear dumbbells such is the case and we have

$$A = -\frac{1}{2}\,n\,k\,T\,\log\,(\det \underline{S}) + \frac{1}{2}\,n\,\kappa\,\mathrm{tr}\,\underline{S} \qquad (3.2\text{-}36)$$

with k = the spring modulus of the dumbbells. The expression (36), first obtained by Grmela and Carreau [6], is ensistent with the Booy-Wiegen [10] expression for the configuration distribution function in the expression (2) of the free energy. The thermodynamic force conjugate with $\underline{S}$ is obtained by differentation of (36).

In this way we get the variable Π at the configuration-tensor level of description:

$$\Pi = \underline{M} = \frac{\partial A}{\partial \underline{S}} = \frac{1}{2} n \kappa \left(\underline{1} - \frac{kT}{\kappa} \underline{S}^{-1}\right) \qquad (3.2\text{-}37)$$

Again, we will show that a matrix representation of the form

$$\begin{bmatrix} \underline{T} \\ \dot{\underline{S}} \end{bmatrix} = \begin{bmatrix} \underline{\underline{\eta}} & : & -\underline{\underline{\Lambda}}^T : \\ \underline{\underline{\Lambda}} & : & \underline{\underline{\beta}} : \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{M} \end{bmatrix} \qquad (3.2\text{-}38)$$

applies and specify the matrix elements $\underline{\underline{\eta}}$, $\underline{\underline{\Lambda}}$ and $\underline{\underline{\beta}}$.
To this end an expression for $\dot{\underline{S}}$ is needed. This may be derived by noting that $\dot{S} = \langle \dot{\underline{q}}\,\underline{q} + \underline{q}\,\dot{\underline{q}} \rangle$ in which $\dot{\underline{q}}$ is given by (23).
If subsequently the result (21) for $\underline{m}$ is used one obtains for the case of linear springs.

$$\dot{\underline{S}} = \underline{L} \cdot \underline{S} + \underline{S} \cdot \underline{L}^T + \frac{4kT}{\zeta} \left(\underline{1} - \frac{\kappa}{kT} \underline{S}\right) \qquad (3.2\text{-}39)$$

From (38) and (39) it follows that

$$\Lambda_{ijkm} = \delta_{ik} S_{mj} + S_{im} \delta_{jk} \qquad (3.2\text{-}40)$$

and

$$\underline{\underline{\beta}} = \frac{4}{n\zeta} \underline{\underline{\Lambda}} \qquad (3.2\text{-}41)$$

The dissipative part of the stress tensor is given by $\underline{T}^D = 2\eta\, \underline{D}$, so analogous to (30) we have $\underline{T}^D = \underline{\underline{\eta}} : \underline{L}$ with

$$\underline{\underline{\eta}} = 2\eta\, \underline{\underline{I}} \qquad (3.2\text{-}42)$$

The reversible part is given by the Kramers form (29) with, in the present case $\underline{f}^I = \kappa\, \underline{q}$, so

$$\underline{T}^R = nkT \left(\frac{\kappa}{kT} \underline{S} - \underline{1}\right) \qquad (3.2\text{-}43)$$

and we see from (38), (40) and (43) that indeed

$$\underline{T}^R = \underline{\underline{\Lambda}}^T : \underline{M} \qquad (3.2\text{-}44)$$

It is important to note that the consistency of the evolution equation (39) and the stress tensor expression (43) is only obtained if the correct expression (36) of the free energy is used. This point (see also Maugin and Drauot [2]) was overlooked by Lhuillier [1] who used a quadratic form for the free energy function $A(\underline{S})$ and arrived

at the conclusion that a convection laws similar to (39) (i.e. based upon the Oldroyd upper convective time derivative $\overset{\nabla}{\underline{S}} = \dot{\underline{S}} - \underline{L} \cdot \underline{S} - \underline{S} \cdot \underline{L}^T$) are incompatible with the Kramers expression of the stress tensor. Instead, Lhuilier obtains $\underline{T}^R = 2 \frac{\delta A}{\delta \underline{S}} \cdot \underline{S}$, the so called Eringen "thermodynamic microstress tensor" as the correct stress tensor expression in this case. We have now seen, however that a consistent structure tensor formulation of the elastic dummbbell model is possible with as well an Oldroyd upper convected derivative in the evolution equation as a Kramers expression for the stress tensor.

3.3 **The rigid dumbbell model**

It is interesting to see how constraints may be incorporated in the present formalism. This will be illustrated now for the rigid dumbbell model. This model is very similar to the elastic dumbbell described in the previous section. The difference is the rigidity constraint: $|\underline{q}| = q = \text{constant}$.
As a consequence the connector force $\underline{f}^I$ is no longer a function of $\underline{q}$, but a constraining force, determined by the equilibrium of forces in the $\underline{q}$-direction. It has been shown [11] that the treatment of the rigidity constraint is facilated, by using the projection operator

$$\underline{P} = \underline{1} - \underline{e}\,\underline{e} \qquad (3.3\text{-}1)$$

with $\underline{e} = \underline{q}/|\underline{q}|$ a unit vector in the direction of $\underline{q}$. We shall see that this operator also plays a prominent role in the present treatment.
We start with configuration-space level of description. Similar to (2) the free energy then becomes:

$$A\{\psi\} = nkT \int \psi \ln \psi \, d^2\underline{e} \qquad (3.3\text{-}2)$$

and the corresponding chemical potential:

$$\mu = \frac{\partial A}{\partial \psi} = nkT \, (1 + \ln \psi) \qquad (3.3\text{-}3)$$

The diffusion equation may analogous to (3.2-7) be expressed as

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial \underline{e}} \cdot (\psi \, \underline{P} \cdot \underline{L} \cdot \underline{e}) + \frac{2}{n \zeta q^2} \frac{\partial}{\partial \underline{e}} \cdot \left(\psi \frac{\partial \mu}{\partial \underline{e}} \right) \qquad (3.3\text{-}4)$$

If a matrix expression similar to (3.2-6) is defined one obtains from (4):

$$\underline{\Lambda} = - \frac{\partial}{\partial \underline{e}} \cdot (\psi \, \underline{P} \, \underline{e}) \qquad (3.3\text{-}5)$$

and

$$\beta = \frac{2}{n\,\zeta\,q^2}\,\frac{\partial}{\partial \underline{e}}\cdot\psi\,\frac{\partial}{\partial \underline{e}} \qquad (3.3\text{-}6)$$

The stress tensor for the rigid dumbbell is given by

$$\underline{T} = 2\eta\,\underline{D} + \tfrac{1}{2}\,n\,\psi\,q^2\,\langle \underline{e}\,\underline{e}\,\underline{e}\,\underline{e}\rangle : \underline{D} + nkT\,\langle 3\,\underline{e}\,\underline{e} - \underline{1}\rangle \qquad (3.3\text{-}7)$$

The first two terms of the r.h.s. consitutes the dissipative stress $\underline{T}^D$, so we have

$$\eta = 2\eta\,\underline{\underline{I}} + \tfrac{1}{2}\,n\,\zeta\,\underline{q}^2\,\langle \underline{e}\,\underline{e}\,\underline{e}\,\underline{e}\rangle \qquad (3.3\text{-}8)$$

The last term in (7) is the reversible stress $\underline{T}^R$. Similar to (3.2-10) it may be proved that also in this case we have

$$\underline{T}^R = \mu * \Lambda \equiv \int \mu\,\Lambda\,d^2\,\underline{e} \qquad (3.3\text{-}9)$$

So, the stress tensor expression (7) is compatible with the formalism of section 2 Analogous to (3.2-14) the matrix formulation of the rigid dumbbell model at the present level of description becomes:

$$\begin{bmatrix} \underline{T} \\ \frac{\partial\psi}{\partial t} \end{bmatrix} = \begin{bmatrix} 2\eta\,\underline{\underline{I}} : & \frac{\partial}{\partial \underline{e}}\cdot(\psi\,\underline{P}\,\underline{e})\,* \\ -\frac{\partial}{\partial e}\,(\psi\,\underline{P}\,\underline{e}) : & \frac{-2}{n\,\zeta\,\underline{q}^2}\,\frac{\partial}{\partial \underline{e}}\cdot\psi\,\frac{\partial}{\partial \underline{e}} \end{bmatrix} \begin{bmatrix} \underline{L} \\ \mu \end{bmatrix} \qquad (3.3\text{-}10)$$

At the $(\underline{T},\underline{L}\ /\ \underline{m},\ \dot{\underline{q}})$ - level of description the thermodynamic force becomes

$$\underline{m} = \frac{\partial\mu}{\partial \underline{\underline{e}}} = k\,T\,\frac{\partial}{\partial \underline{\underline{e}}}\,\ln\psi \qquad (3.3\text{-}11)$$

and the equation of motion is given by

$$\dot{\underline{e}} = \underline{P}\cdot\underline{L}\cdot\underline{e} - \frac{2}{\zeta\,\underline{q}^2}\,\underline{m} \qquad (3.3\text{-}12)$$

If, again, we define the stresslet $\underline{\tau}$ by $\underline{T} = n\,\langle\underline{\tau}\rangle$, from (10) and the stress tensor expression (7) the following matrix representation may be obtained:

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{e}} \end{bmatrix} = \begin{bmatrix} \left(\frac{2\eta}{n}\,\underline{I} + \frac{\zeta\,\underline{q}^2}{2}\,\underline{e}\,\underline{e}\,\underline{e}\,\underline{e}\right) : & -(\underline{P}\,\underline{e})^T\cdot \\ \underline{P}\,\underline{e} : & \frac{2}{\zeta\,\underline{q}^2}\,\underline{1}\cdot \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m} \end{bmatrix} \qquad (3.3\text{-}13)$$

In verifying the equality $\underline{T}^R = n\,\langle\underline{\tau}^R\rangle = n\,\langle\underline{m}\cdot\underline{P}\,\underline{e}\rangle$ it should be noted that

$$\int \frac{\partial\psi}{\partial \underline{e}}\cdot(\underline{1} - \underline{e}\,\underline{e})\,\underline{e}\,d^2\,\underline{e} = -\int \psi\,\frac{\partial}{\partial \underline{e}}\cdot\left[(\underline{1} - \underline{e}\,\underline{e})\underline{e}\right]\,d^2\,\underline{e} = \int \psi\,(3\,\underline{e}\,\underline{e} - \underline{1})\,d^2\underline{e}$$

The result (13) may be brought in a form which is more similar to the elastic dumbbell result (3.2-32) by defining a thermodynamic force

$$\underline{m}_q = \frac{\partial \mu}{\partial \underline{q}} \tag{3.3-14}$$

in which $\eta = \eta\ (\underline{e})$ is an arbitrary extension of the function $\eta(\underline{e})$ to the whole $\underline{q}$ space. Then we have:

$$\underline{m} = \underline{q}\ \underline{P} \cdot \underline{m}_q \tag{3.3-15}$$

If we also use that $\dot{\underline{q}} = \underline{q} \cdot \underline{e}$, (13) may be written as

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{g}} \end{bmatrix} \quad \begin{bmatrix} (\frac{2\eta}{n}\ \underline{I} + \frac{\zeta q^2}{2}\ \underline{e}\ \underline{e}\ \underline{e}\ \underline{e}) : -(\underline{P}\ \underline{q})^T \cdot \\ \underline{P}\ \underline{q} : \qquad\qquad \frac{2}{\zeta}\ \underline{P} \cdot \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m}_q \end{bmatrix} \tag{3.3-16}$$

From (16) the description on the $(\underline{\tau},\ \underline{L}\ /\ \underline{m}_q,\ \underline{q})$-level is readily obtained by writing

$$\underline{\tau} = \underline{f}\ \underline{g} \tag{3.3-17}$$

which follows from the Kirkwood-Kramers expression of the stress tensor [7], and using the fact that $\dot{\underline{d}} = \underline{L} \cdot \underline{g}$.
The result is:

$$\begin{bmatrix} \underline{f} \\ \dot{\underline{q}} \end{bmatrix} = \begin{bmatrix} \frac{\zeta q}{2}\ (\underline{1} - \underline{P}) & -\underline{P} \\ \underline{P} & \frac{2}{\zeta}\ \underline{P} \end{bmatrix} \cdot \begin{bmatrix} \dot{\underline{d}} \\ -\underline{m}_q \end{bmatrix} \tag{3.3-18}$$

Note that the corresponding equation (3.2-34) for the case of elastic dumbbels is obtained if we take $\underline{P} = \underline{1}$

The theory of Doi [12] for nematic liquid crystals may be formulated very similar to equation (16). In that case the viscous stresses are neglected, so the (1,1)-element of the matrix in (16) becomes zero. Furthermore a mean field potential $\Phi(\underline{e})$ is introduced, in order to describe the tendency of the rods to assign in preferred directions. Instead of (11) we then have

$$\underline{m} = kT\ \frac{\partial}{\partial \underline{e}}\ \ln \psi + \frac{\partial}{\partial \underline{e}}\ \Phi \tag{3.3-19}$$

Usually Φ is taken to be the Maier-Saupe potential:

$$\Phi = \text{const} - \frac{3}{2}\ NkT\ \underline{e}\ \underline{e} : \underline{S} \tag{3.3-20}$$

in which $\underline{S}$ is the structure tensor, defined as

$$\underline{S} = \langle \underline{e}\ \underline{e} - \frac{1}{3}\ \underline{1} \rangle \tag{3.3-21}$$

The evolution equation for the rotary motion of the rods is given by [12]

$$\frac{\partial \psi}{\partial t} = - \frac{\partial}{\partial \underline{e}} \cdot (\psi \, \underline{P} \cdot \underline{L} \cdot \underline{e}) + \bar{D}_r \frac{\partial}{\partial \underline{e}} \cdot (\psi \frac{\partial \ln \psi}{\partial \underline{e}} + \psi \frac{\partial}{\partial \underline{e}} \frac{\Phi}{kT}) \qquad (3.3\text{-}22)$$

in which D_r is an average rotary diffusivity.
From this expression we see that

$$\dot{\underline{e}} = \underline{P} \cdot \underline{L} \cdot \underline{e} - \frac{D_r}{kT} \underline{m} \qquad (3.3\text{-}23)$$

which is indeed similar to the expression of $\dot{\underline{e}}$. So we expect that in this case

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{e}} \end{bmatrix} = \begin{bmatrix} \underline{0} & : & -(\underline{P} \, \underline{e})^T \cdot \\ (\underline{P} \, \underline{e}) & : & \frac{\bar{D}_r}{kT} \underline{1} \cdot \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m} \end{bmatrix} \qquad (3.3\text{-}24)$$

In order to prove this, we still have to verify the expression for $\underline{\tau}$, implied by (24). To this end we calculate
$\underline{T} = n \langle \underline{\tau} \rangle = n \langle kT \frac{\partial}{\partial \underline{e}} \ln \psi \cdot (\underline{1} - \underline{e} \, \underline{e}) \underline{e} \rangle + n \langle \frac{\partial \Phi}{\partial \underline{e}} \cdot (\underline{1} - \underline{e} \, \underline{e}) \, \underline{e} \rangle$.

The first term delivers the dilute-solution result $nkT \langle 3 \, \underline{e} \, \underline{e} - 1 \rangle = 3 \, nkT \, \underline{S}$.
For the second term, by using the Maier Saupe potential (20) we obtain
$-3n \, UkT \, (\underline{S} \cdot \underline{S} - \underline{S} : \langle \underline{e} \, \underline{e} \, \underline{e} \, \underline{e} \rangle)$, so

$$\underline{T} = 3 \, nkT \, \underline{S} - 3n \, UkT \, (\underline{S} \cdot \underline{S} - \underline{S} : \langle \underline{e} \, \underline{e} \, \underline{e} \, \underline{e} \rangle \qquad (3.2\text{-}25)$$

This result is indeed in accordance with the stress tensor expression obtained by Doi. So we see that the matrix representation (24) is consistent with the theory of Doi.

In the theory of nematics one often employs the preaveraging assumption.

$$\langle \underline{e} \, \underline{e} \, \underline{e} \, \underline{e} \rangle = \langle \underline{e} \, \underline{e} \rangle \langle \underline{e} \, \underline{e} \rangle \qquad (3.3\text{-}26)$$

In that case a closed description at the $(\underline{T}, \underline{L}/\underline{S}, \underline{M})$ level is possible. Noting that the free energy function corresponding to the Maier-Saupe potential is given by $A_\Phi = - \frac{3}{4} n \, UkT \, \underline{S} : \underline{S}$ we obtain for the thermodynamic force $\underline{M}$:

$$\underline{M} = \frac{\partial A_\Phi}{\partial \underline{S}} = - \frac{3}{2} n \, UkT \qquad (3.3\text{-}27)$$

It can be seen that the equation for $\dot{\underline{S}}$, see ref. [13], obtained from (22) may be re-

presented as

$$\dot{\underline{S}} = \underline{\Lambda} : \underline{L} - \underline{\beta} : \underline{M} \qquad (3.3\text{-}28)$$

with,

$$\underline{\Lambda} : \underline{L} = \tfrac{1}{3}(\underline{L} + \underline{L}^T) + \underline{L} \cdot \underline{S} + \underline{S} \cdot \underline{L}^T - \tfrac{1}{3}(\underline{L} + \underline{L}^T) : \underline{S}\,\underline{1} - (\underline{L} + \underline{L}^T) : \underline{S}\,\underline{S} \qquad (3.3\text{-}29)$$

and,

$$\underline{\beta} : \underline{M} = \frac{4 D_r}{n UkT}\left[(1 - \tfrac{U}{3})\underline{M} - U(\underline{S} \cdot \underline{M} - \tfrac{1}{3}\underline{S} : \underline{M}\,\underline{1}) + U\,\underline{S}\,\underline{S} : \underline{M}\right] \qquad (3.3\text{-}30)$$

From (29) we calculate

$$\underline{\Lambda}^T : \underline{M} = \tfrac{1}{3}(\underline{M} + \underline{M}^T) + \underline{M} \cdot \underline{S} + \underline{S} \cdot \underline{M} - \tfrac{1}{3}(\underline{M} + \underline{M}^T) : \underline{1}\,\underline{S} - (\underline{M} + \underline{M}^T) : \underline{S}\,\underline{S} \qquad (3.3\text{-}31)$$

or by eliminating $\underline{M}$ with (27)

$$\underline{\Lambda}^T : \underline{M} = 3\,n\,kT\,(\underline{S} - U\,\underline{S} \cdot \underline{S} + U\,\underline{S} : \underline{S}\,\underline{S}) \qquad (3.3\text{-}32)$$

Within an isotropic term this is indeed the stress tensor expression, obtained by Doi [13]. So, again the formalism of our triangle model applies. The matrix representation in this case becomes of the form(3.2-38)with $\eta = 0$, $\underline{\underline{\Lambda}}$ and $\underline{\underline{\beta}}$ defined by (29) and (30) and a thermodynamic force $\underline{M}$, given by (27).

3.4 **Reptation models**

The concept of reptation, was proposed originally by de Gennes [14] and used in a rheological model by Doi and Edwards [15] and by Curtiss and Bird [16] in a different way.

We will follow here the approach of Doi and Edwards in which the polymer molecule is treated as a chain, confined in a tube. The tube consists of N segments of a length **a**. The average contour of the molecule coincides with the center line of the tube and is called the "primitive chain". Due to the thermal motion at the molecule the primitiva chain performs a diffusive motion along its own contour (reptation) and tube elements are created and destructed at the endpoints of the primitive chain.

The motion of a primitive chain segment consists of two parts : a convective part and a diffusive part.

The convective part is fully determined by the motion of the tube segments and causes a rate of rotation.

$$\dot{\underline{e}} = \underline{L} \cdot \underline{e} - \underline{e} \cdot \underline{D} \cdot \underline{e} = \underline{P}\,\underline{e} : \underline{L} \qquad (3.4\text{-}1)$$

of the segment-orientation vectors $\underline{e}$. In the second expression (1) we have used the projection operator defined by (3.3-1). The diffusive part of the motion of the segments determines the motion of the chain along the tube. This motion is governed by the diffusion law

$$\dot{s} = - D \frac{\partial \ln \psi}{\partial s} \qquad (3.4\text{-}2)$$

in which D is a diffusion constant, s the curve linear position along the tube and $\psi = \psi(\underline{e}, s, t)$ a probability density for one segment of being at a position s with an orientation $\underline{e}$ at time t. The function ψ may be represented [15] by the integral expression:

$$\psi(\underline{e}, s, t) = \int_{-a}^{t}\int \kappa\,(t - t', s)\,\delta(\underline{e} - \bar{\underline{e}}(e', t', t)\,\hat{\psi}(e')\,d\,\hat{e}'\,dt' \qquad (3.4\text{-}3)$$

in which $\kappa(t - t', s)$ a memory function determined by the diffusion process along the rope, $\bar{\underline{e}}(\underline{e}', t', t) = \underline{F}_t(t') \cdot \underline{e}' / |(\underline{F}_t(t') \cdot \underline{e}'|$ (with $\underline{F}_t(t')$ the relative deformation gradient) a function which determines the relation between the orientation ($\underline{e}'$) of a tube element at the tense of creation (t') and its orientation at the present tense (t) and $\hat{\psi}(\underline{e}')$ is the orientation distribution function of tube elements at the constant of creation.

We also will use the averages of κ along the tube.:

$$\phi(t - t') = \frac{1}{L} \int \kappa(t - t', s)\,ds \qquad (3.4\text{-}4)$$

The calculation of the stress tensor in the Doi and Edwards theory is based upon the expression

$$\underline{T} = n \int_{o}^{L} \langle \sigma\,\underline{e}\,\underline{e} \rangle\,ds \qquad (3.4\text{-}5)$$

in which σ is the tension in the chain. From the theory of rubber elasticity one obtains:

$$\sigma = \frac{3\,kT}{a} \qquad (3.4\text{-}6)$$

If (3) is used to perform the averaging in (5) and (6) is substituted we obtain

$$\underline{T} = 3\,n\,N\,kT \int_{\infty}^{t} \phi(t - t')\,\langle \underline{e}\,\underline{e} \rangle'\,dt' \qquad (3.4\text{-}7)$$

in which < >' denotes an average with respect to the creation distribution function $\psi(e')$. In the derivation of (7) we also have used the definition (4) of ϕ.

We will show now in which way it is possible to formulate the Doi and Edwards theory in the framework outlined in section 2. To that end we have to define for this case the tensor $\underline{\tau}$, the vector $\underline{m}$ and the matrix elements in the expression

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{e}} \end{bmatrix} = \begin{bmatrix} \underline{\underline{\eta}} & -\underline{\underline{\Lambda}}^T \\ \underline{\underline{\Lambda}} & \underline{\beta} \end{bmatrix} \begin{bmatrix} \underline{\underline{L}} \\ -\underline{m} \end{bmatrix} \tag{3.4-8}$$

From (1) we see that

$$\underline{\underline{\Lambda}} = \underline{P}\ \underline{e} \tag{3.4-9}$$

and

$$\underline{\beta} = \underline{0} \tag{3.4-10}$$

Since in the Doi and Edwards theory no dissipative stresses occur, we also have

$$\underline{\eta} = \underline{0} \tag{3.4-11}$$

and remaining problem is to verify that $\underline{\tau} = \underline{\underline{\Lambda}}^T \cdot \underline{m}$ is consistent with the stress tensor expression of Doi and Edwards. To this end, like in our previous examples we use as the thermodynamic force

$$\underline{m} = kT \frac{\partial}{\partial \underline{e}} \ln \psi \tag{3.4-12}$$

With the form (10) of $\underline{\underline{\Lambda}}$ we then have

$$\underline{\tau} = (\underline{P}\ \underline{e})^T \cdot \underline{m} = \underline{m} \cdot \underline{P}\ \underline{e} = \underline{m}\ \underline{e} \tag{3.4-13}$$

Here we have used the expressions (3.3-1) and (13) of $\underline{P}$ and $\underline{m}$ respectively.
By performing the average $\langle\underline{\tau}\rangle$ with the distribution function (3) and comparing the result with the stress tensor expression (7) is may be shown, [note that $\int (\frac{\partial}{\partial \underline{e}} \phi)\ \underline{e}\ d^2\underline{e} = \int (3\ \underline{e}\ \underline{e} - \underline{1})\ \phi\ d^2\ \underline{e})$], that

$$\underline{T} = \frac{m\ N}{L} \int_0^L \langle\underline{\tau}\rangle\ ds + \text{isotropic term} \tag{3.4-14}$$

So we see that the quantity $\underline{\tau}$ introduced above is indeed the appropriate variable to be used in the matrix formulation. We also obtain the following result

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{e}} \end{bmatrix} = \begin{bmatrix} \underline{\underline{0}} & : & -(\underline{P}\ \underline{e})^T \\ (\underline{P}\ \underline{e}): & & \underline{0} \cdot \end{bmatrix} \begin{bmatrix} \underline{\underline{L}} \\ -\underline{m} \end{bmatrix} \tag{3.4-15}$$

It is possible to include the variable s in the the theory. To this end we introduce a thermodynamic force associated with the diffusive motion of the chain. This force is the thermodynamic potential

$$\mu = kT \frac{\partial \ln \psi}{\partial s} \qquad (3.4\text{-}16)$$

The equation (2) may be written then as $\dot{s} = -(D/kt)\,\eta$ and the matrix form (15) becomes:

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{e}} \\ \dot{\underline{s}} \end{bmatrix} = \begin{bmatrix} \underline{0} & : & -(\underline{P}\,\underline{e})^{T} & \underline{0} \cdot \\ (\underline{P}\,\underline{e}) & : & \underline{0} \cdot & \underline{0} \cdot \\ \underline{0} & : & \underline{0} \cdot & \frac{D}{kt} \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m} \\ -\mu \end{bmatrix} \qquad (3.4\text{-}17)$$

We see that μ only contributes to the flux $\dot{s}$ and not to the tensor $\underline{\tau}$.

A generalisation of the Doi and Edwards theory in which frictional forces between the chain and the tube wall were taken into account was presented first by Jongschaap [17] (see also Geurts and Jongschaap [18]). This model, which was called the "Reptating Rope Model" was shown to be equivalent to the theory of Curtiss and Bird. The main difference with the Doi and Edwards theory is an extra term in the stress tensor of the form.

$$\underline{T}^{D} = n\,N\,\frac{\xi}{2}\int_{-\infty}^{t}\int_{0}^{t} s(L-s)\,\kappa(t-t',s)\,\langle \underline{e}\,\underline{e}\,\underline{e}\,\underline{e}\rangle : \underline{D}\,ds\,dt' \qquad (3.4\text{-}18)$$

Comparing this with (14) and (17) we see that the matrix representation of Reptating Rope model becomes:

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{e}} \\ \dot{\underline{s}} \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\xi\, s(L-s)\,\underline{e}\,\underline{e}\,\underline{e}\,\underline{e} & : & -(\underline{P}\,\underline{\dot{e}})^{T} \cdot & \underline{0} \cdot \\ \underline{P}\,\underline{e} & : & \underline{0} \cdot & \underline{0} \cdot \\ \underline{0} & : & \underline{0} \cdot & \frac{D}{kt} \end{bmatrix} \begin{bmatrix} \underline{L} \\ -\underline{m} \\ -\mu \end{bmatrix} \qquad (3.4\text{-}19)$$

Although we now have seen how the triangle model may be applied to reptation models some point remain to be clarified. First we see that a front-factor 3 in the stress tensor expression is obtained. This factor arises from the averaging in orientation space and is similar to the same factor in reversible part of the stress tensor (3.3-13) of the rigid dumbbell model. The factor 3 is also present in the theory of Doi and Edwards but seems to have a different origin there. It does nog appear in the Curtiss Bird theory or in the Reptating Rope Model. The main difference is that in our present formulation the thermodynamic force $\underline{m}$ associated with the orientation distribution of the segments plays a prominent role whereas in the original reptation theories it is the tensile force along the chain which contributes to the stress.

3.5 Transient-Network models

The Transient-Network Model, originally developed by Green and Toblsky [18] Lodge [19] and Yamamoto [20]is used to describe the rheological behaviour of polymer melts and concentrated polymer solutions. In the model, the system of highly entangled polymers is represented by a rubberlike network of segments. The network is not permanent since the segments are created and annihilated at specified rates.

Before describing it in our present formalism we will first briefly summarise some basic notions of the Transient Network Model. The number density $\Psi(\underline{q},t)$ of segments with a specified configuration may, analogous to (3.4-3) be expressed as

$$\Psi = \int_{-\infty}^{t} \int \tilde{n}\ (t,t')\ \ \delta(\underline{q}-\bar{\underline{q}}(\underline{q}',t't))\ \hat{\psi}(\underline{q}')\ d^3\underline{q}'\ dt' \qquad (3.5\text{-}1)$$

In this expression $\tilde{n}(t,t')$ is the number of segments created per unit time at time t' and still present at time t,

$$\bar{\underline{q}} = \underline{F}_t^{-1}(t') \cdot \underline{q}' \qquad (3.5\text{-}2)$$

A function specifying the motion of the segments and $\hat{\psi}(\underline{q}')$ the creation distribution function of a segment which usually is assumed to be afunctional. The equation (2) specifies the assumption of affine motion of the segments. This may also be expressed as

$$\dot{\underline{q}} = \underline{L} \cdot \underline{q} \qquad (3.5\text{-}3)$$

The kinetics of loss and creation of segments may be specified by the properties of the function $\tilde{n}(t,t')$. At constant t', the change of $\tilde{n}$ with t is due to loss. This is expressed by the loss function h(t), defined by

$$\frac{\partial\, \tilde{n}(t,t')}{\partial\, t} = -\ h(t)\ \tilde{n}(t,t') \qquad (3.5\text{-}4)$$

On the other hand $\tilde{n}\ (t',t')\ dt'$ is the number of segments created in the time interval $[t',t' + dt']$, therefore a creation function $g(t')$ is defined by

$$\tilde{n}\ (t',t') = n_o\ g(t') \qquad (3.5\text{-}5)$$

In this expression n_o denotes the equilibrium value of the number density of segments n. The relation between n and $\tilde{n}$ is:

$$n(t)=\int_{-\infty}^{t} \tilde{n}(t,t')\ dt' \qquad (3.5\text{-}6)$$

From this expression and (4) and (5) the following rate equation for n is obtained:

$$\frac{dn}{dt} = g\, n_o - h\, n \qquad (3.5\text{-}7)$$

The solution of (7) with the initial condition (5) may be expressed as

$$\tilde{n}(t,t') = n_o\, g(t,t')\, e^{-\int_{t'}^{t} h(t'')\, dt''} \qquad (3.5\text{-}8)$$

We will now apply the triangle theory to the transient network model like in some of the previous applications we take the one-segment contribution $\underline{\tau}$ to the stress tensor as the stress variable, so

$$\underline{T} = \int \Psi(\underline{q},t)\, \underline{\tau}\, d^3\underline{q} \qquad (3.5\text{-}9)$$

The matrix representation then becomes:

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{q}} \\ \dot{n} \end{bmatrix} = \begin{bmatrix} \underline{0} & -(\underline{1}\,\underline{q})^T & \underline{0} \\ \underline{1}\,\underline{q} & \underline{0} & \underline{0} \\ \underline{0} & \underline{0} & \frac{g}{kT} \end{bmatrix} \begin{bmatrix} -\underline{L} \\ -\underline{m} \\ -\mu \end{bmatrix} \qquad (3.5\text{-}10)$$

with

$$\underline{m} = k\, \underline{q} \qquad (3.5\text{-}11)$$

the spring-force in a segment and

$$\mu = kT\, (\frac{h}{g}\, n - n_o) \qquad (3.5\text{-}12)$$

a chemical potential associated with the change in the free energy of the network due to a change of n. In principle this quantity could be derived form details of the entanglement-desentanglement previous regarded as a chemical reaction, but, following Ajji at al [33], we use the form (12)suggested by the rate equation (7) of the transient network model. The expression for $\underline{\tau}$ obtained form (10) and (11) is in accordance with the usual stress tensor expression $\underline{T} = k \int \Psi\, \underline{q}\, \underline{q}\, d^3\underline{q}$. Substitution of Ψ as given by (1) and making use of (2), and (8) results in the constitutive equation

$$\underline{T} = n_o\, kT \int g(t')\, e^{-\int_{t'}^{t} h(t'')\, dt''}\, \underline{c}_t^{-1}(t')\, dt' \qquad (3.5\text{-}13)$$

in which $\underline{c}_t(\tau) = \underline{F}_t(\tau) \cdot \underline{F}_t\ (\tau)^{-1}$

Returning to the matrix expression (10) we will consider now some possible modifications of the model. First like has been done in the case of the elastic dumbbell model (section 3.1) one may change the level of description. For instance by using the distribution function $\Psi(\underline{e},t)$ or alternatively a structure tensor. $\underline{S} = \langle \underline{q}\, \underline{q} \rangle$ as a state variable. We will not discuss these modifications here. An interesting change

at the present level of description however is a change of the convection law. A well known alternative is the so called Gordon and Schowalter [22] non affine convection law, also used in the Phan Thien-Tanner [23] formulation of the Transient Network Model. In that case instead of (3) we have

$$\dot{\underline{q}} = \underline{L} \cdot \underline{q} - \xi \underline{D} \cdot \underline{q} \qquad (3.5\text{-}14)$$

in which $\underline{D} = \frac{1}{2}(\underline{L} + \underline{L}^T)$, the rate of strain tensor. This may be written as,

$$\dot{\underline{q}} = \left[(1 - \frac{\xi}{2})\ \underline{1}\ \underline{q} - \frac{\xi}{2}\ (1\ \underline{q})^T\right] : \underline{L} \qquad (3.5\text{-}15)$$

The skew symmetry of the matrix in (2.17) then implies that

$$\underline{\tau} = \left[(1 - \frac{\xi}{2})\ (\underline{1}\ \underline{q})^T - \frac{\xi}{2}\ (1\ \underline{q})^T\right] \cdot \underline{m}$$

$$= (1 - \frac{\xi}{2})\ \underline{m}\ \underline{q} + (\text{isotropic term}) \qquad (3.5\text{-}16)$$

This implies that also in the stress tensor expression a factor $(1 - \frac{\xi}{2})$ should be included. The point that in the case of non-affine motion the stress tensor expression should be modified has been discussed in an other context by Larson [24] and also by Maugin and Drout [2] and by Grmela [3]. As pointed out by Larson [24], the physical reason for the extra factor in the stress tensor is some kind of "slip" of the network strands. We will illustrate this now for the case of slip in entanglement. In figure 2 a piece of a polymer chain between two entanglements is shown.

If the forces $\underline{f}$ and $\underline{m}$, and the vectors $\underline{q}$ and $\underline{s}$ are defined as indicated in figure 2. Conservation of energy requires (in the case of no friction in the entanglements) that

$$\underline{f} \cdot \dot{\underline{q}} = \underline{m} \cdot \dot{\underline{s}} \qquad (3.5\text{-}17)$$

So, if we introduce a slip factor **a** by requiring

$$\dot{\underline{s}} = a\ \dot{\underline{q}} \qquad (3.5\text{-}18)$$

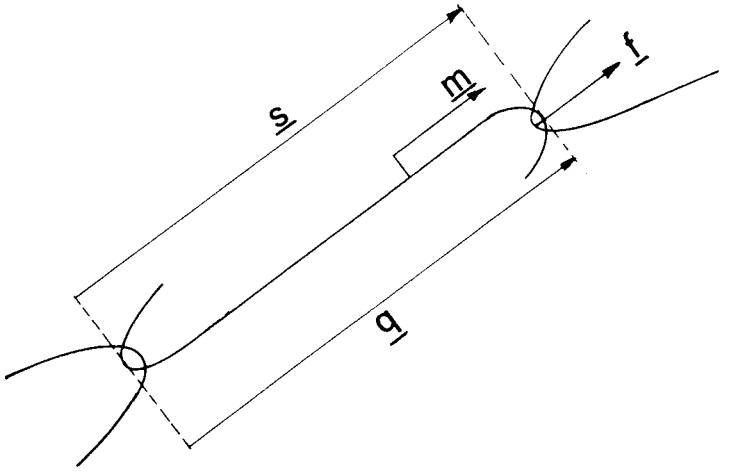
we have,

$$\underline{m} = \frac{1}{a}\ \underline{f} \qquad (3.5\text{-}19)$$

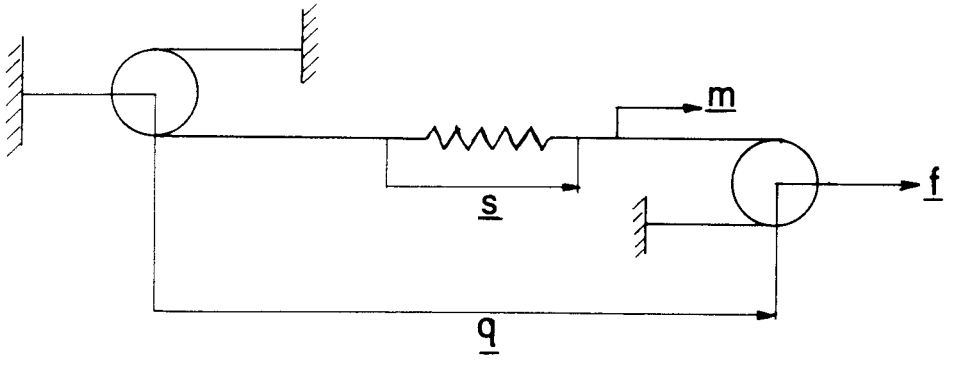
(In the case represented by Figure 2b we would have a = 2.) The stress tensor in a network corresponding to the entanglement structure of Figure 2*a* would become. $\underline{T} = n\langle \underline{f}\ \underline{q}\rangle = n\ a\langle \underline{m}\ \underline{q}\rangle$. If in this expression we take $\underline{m} = \kappa\ \underline{s}$ with $\underline{s} = \underline{q}$ (since at any instant the total part of the chain between two entanglements contributes to the elastic stress), we obtain,

$$\underline{T} = n\kappa\ a\langle \underline{q}\ \underline{q}\rangle \qquad (3.5\text{-}20)$$

in accordance with our previous result (16).



(a)



(b)

Figure 2

Non affine motion due to slip in entanglements : schematic picture of the entanglement structure (*a*) and mechanical analogue (b). The chain vector $\underline{s}$ of a part of the chain changes at rate that differs from the rate of change of the vector $\underline{q}$ between two entanglements. The elastic force $\underline{m}$ in the chain also differs from the force $\underline{f}$, acting upon the entanglements.

Also in this case the situation may be clearly summarised in a matrix representation. At the $(\underline{f},\dot{\underline{q}}/\underline{m},\dot{\underline{s}})$ - level we have

$$\begin{bmatrix} \underline{f} \\ \dot{\underline{s}} \end{bmatrix} = \begin{bmatrix} \underline{0} & -a \\ a & \underline{0} \end{bmatrix} \cdot \begin{bmatrix} \dot{\underline{q}} \\ -\underline{m} \end{bmatrix} \qquad (3.5\text{-}21)$$

and at the $(\underline{\tau},\underline{L}/\dot{\underline{s}},\underline{m})$ - level :with $\underline{\tau} = \underline{f}\ \underline{q}$

$$\begin{bmatrix} \underline{\tau} \\ \dot{\underline{s}} \end{bmatrix} = \begin{bmatrix} \underline{0} & -(a\ \underline{1}\ \underline{q})^T \\ a\ \underline{1}\ \underline{q} & \underline{0} \end{bmatrix} \begin{bmatrix} \underline{L} \\ \underline{m} \end{bmatrix} \qquad (3.5\text{-}22)$$

3.6 Configuration tensor models

In the case of the elastic dumbbell model (section 3.1) we have seen an example in which a closed formulation of the theory is possible at the $(\underline{T},\underline{L}/\underline{M},\underline{S})$ - level. In that case the structure tensor $\underline{S}$ was defined by (3.2-35) in terms of microscopic variables and its properties were derived from the underlying configuration-space theory. In some cases, it may be usefull to introduce the properties of the structure tensors without an explicit reference to molecular theories. This possibility - in fact - is the main advantage of the use of different levels of description in combination with a consistent thermodynamic formulation.

A nice example of a structure tensor theory which is a model proposed by Giesekus [27,28]. In this theory, which may be considered as a generalisation of the elastic dumbbell model described in section 3.2.the reversible part of the stress tensor is assumed to be of the form

$$\underline{T}^R = \mu(\underline{C} - \underline{1}) \qquad (3.6\text{-}1)$$

This expression is consistent with our previous result (3.2-43) if we take $\mu = nkT$ and $\underline{C} = \frac{\kappa}{kT}\underline{S}$.

For the tensor $\underline{C}$, the following evolution equation is proposed:

$$\overset{\nabla}{\underline{C}} = -\underline{B} \cdot \underline{T}^R \qquad (3.6\text{-}2)$$

with $\overset{\nabla}{\underline{C}} = \dot{\underline{C}} - \underline{L} \cdot \underline{C} - \underline{C} \cdot \underline{L}^T$, the upper convected derivative, and $\underline{B}$ a kind of generalized mobility tensor which is taken to be

$$\underline{B} = \beta(\underline{1} + a\ \underline{T}^R) \qquad (3.6\text{-}3)$$

In order to compare this with our previous results we note that from

$$\dot{\underline{C}}^R = \underline{L} \cdot \underline{C} + \underline{C} \cdot \underline{L}^T = \underline{\underline{\Lambda}} : \underline{C} \qquad (3.6\text{-}4)$$

in which $\underline{\underline{\Lambda}}$ is of the same form (3.2-40) as in the dumbbell model. With this expression for $\underline{\underline{\Lambda}}$, on using the result $\underline{T}^R = \underline{\underline{\Lambda}}^T : \underline{M}$ we obtain from (1) that

$$\underline{M} = \frac{1}{2}\mu\ (\underline{1} - \underline{C}^{-1}) \qquad (3.6\text{-}5)$$

which is indeed in accordance with (3.2-37)

The tensor $\underline{\underline{\beta}}$ in the expression $\dot{\underline{C}}^B = -\underline{\underline{\beta}} : \underline{M}$ may be obtained now by using the result $\dot{\underline{C}}^D = -\underline{B} \cdot \underline{T}^R$, which follows from (2) and the expressions (1), (3) and (5) for $\underline{T}^R$, $\underline{B}$ and $\underline{M}$. The result is

$$\underline{\underline{\beta}} = -\underline{B} \cdot \underline{\underline{\Lambda}} \qquad (3.6\text{-}6)$$

If this is compared with the elastic dumbbell result (3.2-41) one sees that the tensor $\underline{B}$ generalizes the mobility factor $4/n\,\xi$. In the case that a = 0 the elastic dumbbell result is reobtained. The viscous stress in the Giesekus model has the usual form $\underline{T}^D = \underline{\underline{\eta}} : \underline{L}$ with $\underline{\underline{\eta}}$ given by (3.2-42), so the model may be summarizes now as follows:

$$\begin{bmatrix} \underline{T} \\ \dot{\underline{C}} \end{bmatrix} = \begin{bmatrix} 2\eta\,\underline{\underline{I}} & -\underline{\underline{\Lambda}}^T \\ \underline{\underline{\Lambda}} & \underline{B} \cdot \underline{\underline{\Lambda}} \end{bmatrix} : \begin{bmatrix} \underline{L} \\ -\underline{M} \end{bmatrix} \qquad (3.6\text{-}7)$$

with $\underline{\Lambda}$, $\underline{B}$ and $\underline{M}$ given by (3.2-40), (3) and (5) respectively. By elimination of $\underline{M}$, $\underline{C}$ and $\dot{\underline{C}}$ the following constitutive equations may be obtained:

$$\underline{T}^D = 2\,\eta\,\underline{D} \qquad (3.6\text{-}8)$$

$$\underline{T}^R + \lambda\,\overset{\nabla R}{\underline{T}} + a\,\underline{T}^R \cdot \underline{T}^R = 2\,\beta^{-1}\,\underline{D} \qquad (3.6\text{-}9)$$

with $\lambda = \dfrac{1}{\beta\,\eta}$.

The Giesekus model is a good illustration of how a slight modification of the dumbbell model, expressed at the configuration-tensor level of description may cause signigicant changes in the constitutive equations.

In the Giesekus model, the treatment was partially based upon the underlying molecular description. In other models at the configuration- tensor-level the approach is entirely at a macroscopic level. An example is the theory of Leonov [25] based upon the concept of a recoverable strain and theories based upon Eckarts [29] concept of a variable relaxed state. For further information about the latter class of theories we refer to a paper by Stickforth [30]. For our present discussion it is sufficient to know that in those theories the stress and the velocity gradient are decomposed in a reversible (elastic) and a dissipative (inelastic) part.

So we have like before : $\underline{T} = \underline{T}^R + \underline{T}^D$ but also : $\underline{L} = \underline{L}^R + \underline{L}^D$. In order to compare this with our formalism we have to define $\underline{L}^R$ and $\underline{L}^D$ in a consistent way. to this end we rewrite the dissipation form as follows

$$\begin{aligned} \Delta &= \underline{T} : \underline{L} - \underline{M} : \dot{\underline{S}} \\ &= \underline{T} : \underline{L} - \underline{M} : \underline{\underline{\Lambda}} : \underline{\underline{\Lambda}}^{-1} : \dot{\underline{S}} \\ &= \underline{T} : \underline{L} - \underline{T}^R : \underline{L}^R \end{aligned} \qquad (3.6\text{-}10)$$

in which (3.2-44) has been used and

$$\underline{L}^R = \underline{\underline{\Lambda}}^{-1} : \dot{\underline{S}} \qquad (3.6\text{-}11)$$

Instead of (10) one may also write

$$\Delta = \underline{T}^D : \underline{L} + \underline{T}^R : \underline{L}^D \qquad (3.6\text{-}12)$$

The phenomenological relations according to non-equilibrium thermodynamics then become :

$$\begin{bmatrix} \underline{T}^D \\ \underline{L}^D \end{bmatrix} = \begin{bmatrix} \underline{\underline{\eta}} & -\underline{\underline{\Phi}}^T \\ \underline{\underline{\Phi}} & \underline{\underline{\upsilon}} \end{bmatrix} : \begin{bmatrix} \underline{L} \\ -\underline{T}^R \end{bmatrix} \qquad (3.6\text{-}13)$$

This, indeed, is the form obtained by Leonov [25], Stickforth [27] and others. In our present approach, however, it is possible to go one step further. If we start from our matrix expression (3.2-38)and eliminate $\underline{M}$, $\underline{S}$ and $\underline{T}$ in the same way as in deriving(13), we obtain :

$$\begin{bmatrix} \underline{T}^D \\ \underline{L}^D \end{bmatrix} = \begin{bmatrix} \underline{\underline{\eta}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{\upsilon}} \end{bmatrix} : \begin{bmatrix} \underline{L} \\ -\underline{T}^R \end{bmatrix} \qquad (3.6\text{-}14)$$

with $\underline{\underline{\upsilon}} = \underline{\underline{\Lambda}}^{-1} : \beta : \underline{\underline{\Lambda}}^{-T}$ which is of the same form as (13) but with one important difference, namely that the matrix now has the diagonal form. The meaning of the variables $\underline{L}^R$ and $\underline{L}^D$ becomes more clear in a schematic representation similar to the triangle model given in Figure 3. We see that $\underline{L}^R$ and $\underline{L}^D$ correspond to a mapping of the spring and dashpot inside the system. In the case that $\underline{\underline{\Lambda}} = \underline{\underline{1}}$, $\underline{L}^R$ coincides with $\dot{\underline{S}}$ and $\underline{T}^R$ with $\underline{M}$. In other cases these quantities will differ from each other.
From figure 3 it can also be seen that the strain corresponding to $\underline{L}^R$ is indeed the so called recoverable strain, used in the Leonov Model: it is an elastic recovery measured at the part of the system where the external variables $\underline{T}$ and $\underline{L}$ apply.

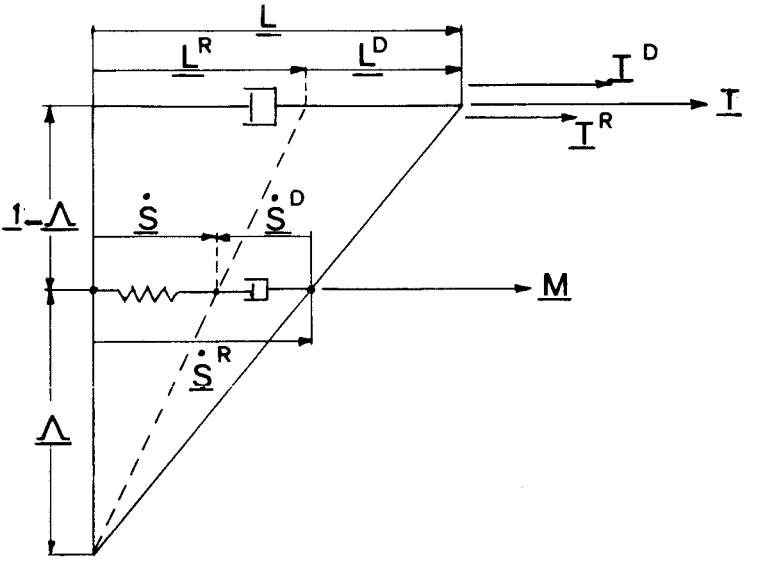


Figure 3
Representation of the model described by the equations (3.2-38) and (3.6-14) by the triangle model (see also Figure 1)

4. Discussion

In this paper a theory was presented by which a unified treatment of various rheological models is possible. The theory may be considered as an extension of earlier work by Grmela [3] and others [1,2]. In our treatment the concept of a so called macroscopic time reversal played a central role. On the basis of this, an unambigious distinguishment between reversible and dissipative variables was possible and a universal matrix representation (2.17) could be given. The skew symmetry of this matrix is in accordance with the Onsager-Casimir symmetry relations.

In the applications, discussed in section 3, we have seen that this skew-symmetry may be used as a check on the consistency of the stress tensor expression with the evolution equation of a model. In the network models with non-affine motion (sec. 3-6), for instance, it implies the necessity of an extra factor in the stress tensor expression. In configuration tensor models the skew symmetry of the matrix in (2.17) may be used to construct the stress tensor expression, from a given evolution equation. In section 3 some examples were given of application of our formalism to existing models. Our purpose there was not to obtain new results in the sense of new constitutive equations, but merely to demonstrate the capability and flexibility of the new approach. Only in the treatment of the dumbbell models (section 3.2 - 3.3) the level of description with functions as state variables and functional dependences was employed. In the other applications a tensor-formulation was sufficient. Nevertheless one should keep in mind that in future applications a functional formulation might be necessary. For instance in cases where nonlocal phenomena are important. The description could be based upon global fields instead of local variables of state ; this makes a functional formulation necessary. In this context the problem of the effects of domains on orientation and stress liquid crystals might be of interest. In the examples of section 3, in most cases only a reformulation of existing theories was obtained. The main advantage of the present formulation, however is it shows in which directions modifications of the model are possible and also that those modifications fall into a few categories. Referring to the general equation (2.17) we first have : a change in the free energy functional $A(\Phi)$ and so of the expression for the thermodynamic stress : $M(\Phi)$, seemed of the viscous effects described by the quantities η and β and third a change of the coupling effect, expressed by the quantity Λ. It has been shown that the latter 4.1 changes significant in the case of constraints and in the case of non-affine motion. So we see that our theory offers the possibility of analysing the implications of particular modifications of a model in a systematic and consistent manner.

In applying the theory to existing models sometimes new insight is obtained. For instance, in the case of the Doi and Edwards model, where we haven seen that the

stress is due to the thermodynamic force associated with the orientation of the tube segments, rather than a tensile force along the tube. We also have clarified the origin of the extra factor in the stress tensor expression due to non-affine motion. Finally, in section 3.7 we arrived at the result that the matrix (3.6-13) in the theory of Leonov and in similar theories should be diagonal.

The use of different levels of description was only fully employed in the case of the elastic dumbbell model. In some other cases this could also be done, but we did not make an attempt to be complete here. Still it should be stressed that a change of level of description result in a considerable simplification of the problem. An obvious case is of course the change from the configuration space level to the structure tensor level of description. The opposite change from the configuration space level to the level of forces and deformations of individual particles, however, is in many cases even more usefull. At this level, in fact, many of the examples that we have considered were formulated. In general one could say that our triangle modelcan be applied in any case in which a thermodynamic subsystem can be defined for which the free energy may be expressed as a function of functional of some state variables, a set of external variables by which the exchange of power with the environment is described and an evolution equation of the microstructure.

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